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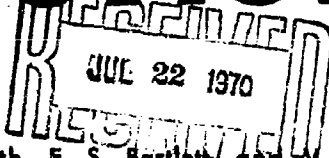
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# review

OF RECENT  
DEVELOPMENTS



## Refractory Metals

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### COLUMBIUM ALLOYS

The parameters required to form beaded heat-shield panels of the Cb-752 and WC-129Y alloys in a thickness of 0.012 inch were described in two reports by General Dynamics.<sup>(1,2)</sup> The evaluations included (1) a fairly extensive series of room-temperature tensile tests to determine the effects of tensile strain- and stress-relieving treatments on the uniform percent elongation of both alloys and (2) the development of tooling and ambient-room-temperature fabrication methods to form the panels desired.

The strain tests showed both alloys work hardened appreciably after tensile prestraining at levels of 8 to 10 percent elongation. Stress relieving these materials after 10.5 to 12 percent pre-strain increased the available ductility for forming.

Beaded panels of both alloys were readily formed using hydropress equipment and the Verson-Wheelon press. Female die forming was necessary to avoid buckling of the 0.012-inch-thick panels in the initial forming stages. Additional forming stages continued in male dies. Best results were obtained by interposing the workpiece between a 0.012-inch-thick caul sheet of Type 321 stainless steel and the forming force. Teflon films of 2-mil thickness were found effective as a die lubricant. A "picture-frame" type of pressure plate over the panel border, with the opening close to the bead configurations, was regarded as a key factor in the prevention of buckles during forming.

The finished columbium alloy panels were about 12.4 by 15.7 inches in size, and each contained 9 parallel bead corrugations about 0.9 inch wide by 10.5 inches long. Bead heights of about 0.31 inch were formed in the single annealed Cb-752 sheet without stress relief between forming stages. The maximum forming stretch was 12 percent in 1 inch. The WC-129Y panels were formed with bead heights in the range of 0.35 to 0.37 inch after stress relief between forming stages. The maximum stretch was 17 percent in 1 inch.

A single panel of the WC-103 columbium alloy was also formed using the same procedures.<sup>(1)</sup> This panel, which had bead heights from 0.33 to 0.38 inch, was formed with greater ease than with either the Cb-752 or WC-129Y alloys. Thus, with WC-103 material, beads with 12 percent maximum stretch in the female die were possible to form,

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whereas 8 to 10 percent stretch was observed in this die with the other alloys. However, excessive "orange peel" was observed in the WC-103 material surface at the highest points of strain, indicating the desirability of stress relieving prior to a 12 percent stretch.

In continuing studies of columbium alloys at the Bureau of Mines, columbium-hafnium-tungsten alloys containing up to 10 atom percent boron were investigated.<sup>(3)</sup> In columbium-hafnium alloys, up to 5 atom percent boron additions appeared to benefit fabricability. Likewise, in ternary columbium-hafnium-tungsten alloys, alloys containing 2 atom percent boron were apparently more fabricable than boron-free alloys, but higher boron contents impaired fabricability. In the annealed condition (1 hour at 1200 C or 2190 F), boron did not contribute to hot strength and quite definitely degraded oxidation resistance as evaluated by weight change.

### COLUMBIUM AND TANTALUM ALLOYS

Studies are in progress at Oak Ridge National Laboratory to strengthen refractory alloys at high temperatures through the precipitation of stable phases.<sup>(4)</sup> Initially, the room-temperature precipitation hardening associated with eutectoid transformations in the tantalum-hafnium (eutectoid temperature of 1050 C or 1920 F) and columbium-zirconium (eutectoid temperature of 610 C or 1132 F) systems was determined on samples of the Ta-50Hf and Cb-58Zr (weight percent) alloys, respectively. Appreciable hardening in the Ta-50Hf alloy was indicated. Thus, the hardness of the solution-treated alloy increased from a value of 460 DPH to a peak hardness of about 790 DPH on aging at 850 C (1560 F) for about 10 minutes. For the Cb-58Zr alloy, only small hardness increases (about 20 DPH) were associated with aging a solution-treated alloy sample at 500 C (930 F); hardness of the solution-treated alloy was about 290 DPH.

### TUNGSTEN ALLOYS

A comparison of the creep-rupture properties of arc melted (AM) and powder-metallurgy (PM) W-25Re sheet has been reported by Oak Ridge investigators.<sup>(5)</sup> Both types of material were compared at 1650 C and 2200 C (3000 and 3990 F) for rupture times to 1000 hours. At comparable stresses, the PM material has a shorter rupture life and lower rupture ductility than AM material. On the basis of secondary creep rate, PM material is weaker than AM material at

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1650 C but stronger at 2200 C. Optical and electron metallography showed that voids form at grain boundaries in both materials. In the PM material, grain boundaries appear to be immobile, and massive growth of voids initiates fracture with very little deformation. In the AM material, grain boundaries appear to be mobile and fracture seems to be forestalled by their ability to move. The relative creep rates can be explained on the basis of void growth and grain size.

In a series of studies at Lewis Research Center in which turbine-bucket applications were simulated, tungsten-alloy fibers were incorporated in Ni-25W-15Cr-2Al-2Ti nickel-base alloy by a slip casting-isostatic hot pressing procedure and the resultant structures were evaluated for stress-rupture strength and oxidation and impact resistance.<sup>(6)</sup> The following alloys and wire diameters were investigated: W-2ThO<sub>2</sub> (0.015 inch and 0.010 inch), W-5Re-2ThO<sub>2</sub>, and W-1ThO<sub>2</sub> (both 0.020 inch) and 218 CS W (0.015 inch). The W-5Re-2ThO<sub>2</sub> wire had the greatest tensile strength of all wires at 2000 F and was comparable to W-2ThO<sub>2</sub> at 2200 F. In stress-rupture tests both diameters of W-2ThO<sub>2</sub> wire proved to be strongest. Subsequent 100-hour stress-rupture tests at 2000 F in which 70 volume percent of wires were incorporated in the superalloy matrix yielded favorably high strength levels, e.g., 49 ksi as compared with 11.5 ksi for the best cast nickel alloys. Standard nickel-base alloys used for turbine-bucket applications have a stress-density value of about 60,000 inches for a 1000-hour rupture life at 1800 F. As illustrated in Figure 1, which takes into account their densities, the nickel alloy W-2ThO<sub>2</sub>-wire combination yielded a 200 F advantage at 1000 hours. The impact strengths as gaged by preliminary tests were comparable to those of cast superalloys. Exposed fiber ends apparently would need some sort of protection against oxidation in service environments.

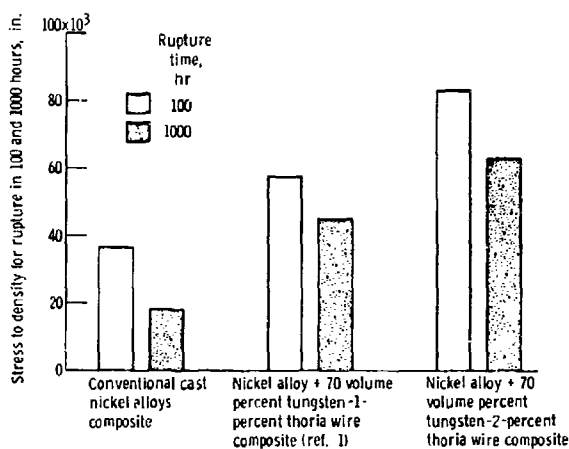


FIGURE 1. 100- AND 1000-HOUR SPECIFIC RUPTURE STRENGTHS OF CAST NICKEL ALLOY AND TUNGSTEN-THORON WIRE-REINFORCED NICKEL ALLOY COMPOSITES TESTED AT 2000 F<sup>(6)</sup>

#### CHROMIUM WIRE

Improved procedures for the preparation of pure chromium wire have been described by workers at the Australian Aeronautical Research Laboratories.<sup>(7)</sup> Briefly, these involve

- (1) Canning the 10-pound, 3-inch-diameter arc-melted ingots in mild steel
- (2) Extrusion at 1200 C (2190 F) to 5/8-inch-diameter rod
- (3) Removal of the steel by machining to 1/2-inch-diameter rod
- (4) Swaging at 900 C (1650 F) to 0.220-inch diameter
- (5) Straightening and grinding to 0.190-inch diameter
- (6) Vacuum annealing at 950 C (1740 F)
- (7) Electropolishing and electroplating with nickel (0.1 to 0.2 mil), then copper (about 2 mils)
- (8) Vacuum annealing 1 hour at 750 C (1380 F)
- (9) Drawing, using a graphitic lubricant at 350 C (660 F).

In the final drawing stage, reductions in area as high as 99.7 percent were possible without intermediate annealing. Under these conditions, a room-temperature tensile strength of about 230 ksi was achieved in 10-mil-diameter wire, along with a yield strength of about 163 ksi and an elongation of about 2 percent. On annealing, recovery and/or recrystallization commenced at 300 C (570 F) but was completed only at 950 C (1740 F).

Wide-ranging combinations of room-temperature strength (110 to 230 ksi) and ductility (2 to 40 percent elongation) were achieved by annealing between 600 and 800 C (1110 to 1470 F).

#### REFRACTORY METALS, GENERAL

Two more reports\* have been issued by Man-Labs on a comprehensive program aimed at characterizing the stability of a wide variety of refractory materials in air under high-velocity conditions. This program has included oxidation studies on refractory borides, graphites and JT composites, hypereutectic carbide-graphite composites, refractory metals (coated and uncoated), metal-oxide composites, and iridium-coated graphites. A principal goal of this program is elucidation of the relationship between hot gas/cold wall (HG/CW) and cold gas/hot wall (CG/HW) surface effects in terms of heat- and mass-transfer rates at high temperatures.

One of these reports concerns a theoretical correlation of material performance with stream conditions.<sup>(8)</sup> Here, published arc-plasma test data

\*The first four reports on this program were described and referenced in the Review of April 10, 1970.

for refractory materials taken in eight different facilities were collected and examined by comparing the observed surface temperatures with calculated radiation-equilibrium values. Included are data for uncoated Hf-20Ta-2Mo, selected iridium alloys, and unalloyed tungsten (forged and as sintered) as well as tungsten which had been infiltrated with copper, zinc, and silver. Coated refractory-metal systems included are  $WSi_2/W$ , Sn-Al/Ta-10W, and W3/T2M. Wide variations in the ratio of calculated to observed temperature were encountered. Similar calculations performed for tests conducted in the present program yielded results close to unity, especially when melting is encountered. Larger ratios (up to 1.5) were noted for specific materials which produce silicon oxides, implying enhanced resistance to energy absorption. Thus, an alternative method of presentation was developed which compares recession rate as a function of heat flux and enthalpy. This provides a means for comparing the performance for various trajectories by applying a flux/enthalpy-altitude/velocity translation in considering candidate materials. For example, comparison of the trajectory of the FGL-7MC lifting reentry vehicle eliminated all of the candidate materials from the nose-cone application except the boride composites.

The second of these reports was aimed toward the analytical formulation of a general surface-reaction description of the mass- and heat-transfer effects for a material body under hypersonic flight conditions.(9)

In a study of potential thermionic materials, Gulf General Atomic determined interdiffusion rates in the binary-alloy systems of tungsten with tantalum, molybdenum, and columbium over the range of 2000 to 2200 C (3630 to 3990 F).(10) In general, the diffusion rates were found to increase in the order of tantalum, molybdenum, and columbium, respectively. The vacuum work functions of the W-2Mo, W-5Re, and W-25Re alloys at 1800 C (3270 F) were also determined as 4.39, 4.69, and 4.77 eV (electron volts), respectively.

Aerojet-General has reported the results of an investigation of the phase relationships in two binary systems, tantalum-nitrogen and hafnium-nitrogen, and of the ternary tantalum-hafnium-nitrogen system.(11) For the latter, isothermal sections from 1000 to 3200 C (1830 to 5790 F) are presented along with an isometric view of this ternary system from room temperature through 3200 C.

#### NEW PROGRAMS

Avco has issued its first progress report on an Army program exploring the feasibility of investment casting of columbium alloys.(12) In this program, castings are being prepared by the REM Metals Corporation using consumable electrodes of WC-3015 and B-66 alloy compositions. These are skull melted and poured into molds in which initial tungsten-slurry dips provide the nonoxidic surface; a backup layer of zirconia is added as the final step in mold manufacture. Thirty-four molds are scheduled in the program to optimize the shell design, mold preheat temperatures, and to produce usable castings for the properties-testing phase. The mold configurations to be used include a fluidity test pattern, stress-rupture bars, oxidation-thermal fatigue paddles, and a Lycoming first-stage

T55 turbine-nozzle vane. To date, threaded test-bar shapes of both alloys have been prepared which show acceptable surface quality and soundness.

Under a new Navy contract, the IIT Research Institute is extending its previous work with oxidation-resistant hafnium alloys.(13) Major emphasis is to be placed on the investigation of selected hafnium-tantalum base alloys as oxidation-resistant claddings for high-strength columbium and tantalum alloys. Thus, two alloys developed in earlier programs (i.e., Hf-24.5Ta-1.2Cr-0.65B-0.12Al and Hf-23.5Ta-1.8Cr-1.1Si) are being prepared as 0.040-inch-thick sheet which will be used to clad substrates of the Cb-752 and Ta-10W alloys, respectively. The oxidation resistance of these composites at 2200 to 2700 F is to be determined as well as their mechanical properties after exposure at these temperatures. Secondary emphasis is being placed on the development of columbium-based alloys containing up to 50 weight percent hafnium with the objective of obtaining high-strength alloys having moderate to good oxidation resistance at 2200 to 2500 F.

#### REFERENCES

- (1) Carpenter, S. R., "Forming and Joining Developments for Columbium and TD NiCr, Radiative Heat Shields", Report GDC-ERR-1344, Convair Division, General Dynamics Corporation, San Diego, Calif. (December 1968).
- (2) Carpenter, S. F., "Fabrication Developments of High-Temperature Materials: Columbium and TD NiCr", Report GDC-ERR-1458, Convair Division, General Dynamics Corporation, San Diego, Calif. (December 1969).
- (3) Babitzke, H. R., Oden, L. L., and Kelly, H. J., "Columbium Alloy Development with Boron, Hafnium, and Tungsten", Report RI 7388, U.S. Bureau of Mines, Albany, Oreg. (June 1970).
- (4) Preliminary information from Union Carbide Corporation, Oak Ridge National Laboratory, Oak Ridge, Tenn., on US AEC Contract W-1405-eng-26, Report ORNL-4480.
- (5) Stephenson, R. L., "Comparative Creep-Rupture Properties of W-25%Re Consolidated by Arc Melting and Powder Metallurgical Techniques", Report ORNL-TM-2651, Oak Ridge National Laboratory, Oak Ridge, Tenn. (September 1969).
- (6) Petrusek, D. W., and Signorelli, R. A., "Preliminary Evaluation of Tungsten Alloy Fiber-Nickel-Base Alloy Composites for Turbojet Engine Applications", Report NASA TN D-5575, NASA, Lewis Research Center, Cleveland, O. (February 1970).
- (7) Henderson, F., Bullen, F. P., and Wain, H. L., "The Preparation and Tensile Properties of Chromium Wire", Report ARL/MET. 64, Aeronautical Research Laboratories, Australian Defence Scientific Service, Melbourne, Australia (March 1969).

- (8) Kaufman, L., et al, "Stability Characterization of Refractory Materials Under High Velocity Atmospheric Flight Conditions - Part IV, Volume I: Theoretical Correlation of Material Performance with Stream Conditions", Report AFML-TR-69-84, Part IV, Volume I, ManLabs Incorporated, Cambridge, Mass., Contract AF 33(615)-3859 (December 1969).
- (9) Bernstein, H., and Baron, J. R., "Stability Characterization of Refractory Materials Under High Velocity Atmospheric Flight Conditions - Part IV, Volume II: Calculation of the General Surface Reaction Problem", Report AFML-TR-69-84, Part IV, Volume II, ManLabs Incorporated, Cambridge, Mass., Contract AF 33(615)-3859 (December 1969).
- (10) Hudson, R. G., Hornes, M. H., and Yang, Y. L., "Some Investigations of Refractory Metal Systems of Thermionic Interest", Report GA-9495, Gulf General Atomic Incorporated, San Diego, Calif., Contracts NAS 3-4165, NAS 3-8504, and AT(04-3)-167 (November 1969).
- (11) Booker, P. H., and Brukl, C. E., "Phase Equilibria Investigation of Binary, Ternary, and Higher Order Systems" - Part VI. The Phase Equilibria in the Metal-Rich Region of the Hafnium-Tantalum-Nitrogen System", Report AFML-TR-69-117, Part VI, Aerojet-General Corporation, Sacramento, Calif., Contract AF 33(615)-67-C-1513 (December 1969).
- (12) Preliminary information from Avco Lycoming Division, Avco Corporation, Stratford, Conn., on U.S. Army Contract DAAG46-69-C-0163.
- (13) Preliminary information from IIT Research Institute, Chicago, Ill., on U.S. Navy Contract N00019-70-C-0120.

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